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APPLICATION NUMBER: 60/509,892

FILING DATE: October 09, 2003

PRIORITY DOCUMENT

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FEE RECORD SHEET

10/15/2003 LWNDIM1 00000046 082336 60509892
01 FC:1005 160.00 DA

PTO-1556
(5/87)


PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No.

ER132926924US

00746 U.S. PTO
-60/509892

INVENTOR(S)					
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<input type="checkbox"/> Additional inventors are being named on the _____ separately numbered sheets attached hereto					
TITLE OF THE INVENTION (500 characters max)					
PROCESS FOR THE ISOMERIZATION OF METALLOCENE COMPOUNDS					
Direct all correspondence to: CORRESPONDENCE ADDRESS					
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ENCLOSED APPLICATION PARTS (check all that apply)					
<input checked="" type="checkbox"/> Specification Number of Pages		18		<input type="checkbox"/> CD(s), Number	
<input type="checkbox"/> Drawing(s) Number of Sheets				<input type="checkbox"/> Other (specify)	
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76					
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT					
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.				FILING FEE AMOUNT (\$)	
<input type="checkbox"/> A check or money order is enclosed to cover the filing fees					
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number:				08-2336	
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.					
<input checked="" type="checkbox"/> No.					
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____					

Respectfully submitted,

SIGNATURE

William R. Reid

Date 10/09/2003

TYPED or PRINTED NAME

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REGISTRATION NO.
(if appropriate)
Docket Number:

47,894

TELEPHONE

410-996-1783

FE 6135 (US)

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

EXPRESS MAILING CERTIFICATE

This certifies that the attached Form PTO/SB/16 (in duplicate),
Specification (18 pages) for the provisional application of **Simona Guidotti et al.,**
PROCESS FOR THE ISOMERIZATION OF METALLOCENE
COMPOUNDS (our ref: **FE 6135 (US)**) is being mailed by "Express Mail Post
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PROCESS FOR THE ISOMERIZATION OF METALLOCENE COMPOUNDS

The present invention relates to a process for the conversion of the meso or meso-like form of a metallocene compound to the corresponding racemic or racemic-like form. The meso or the meso-like form to be subjected to the process of the invention can be admixed with the
5 corresponding racemic (rac) or racemic-like form.

Metallocene compounds are well known complexes, mainly used as catalyst components for the polymerization of olefins. Processes for the synthesis of such metallocene compounds tend to produce mixtures of racemic and meso form. Usually the racemic form produces stereoregular polymers while the meso form is inactive or produces low molecular weight atactic
10 polymers. The racemic form is therefore the most used as polymerization catalyst component. Consequently it is desirable to obtain from the synthesis the racemic (rac) form or a mixture where the racemic form is predominant in order to reduce the work for the physical separation of the two isomers.

EP 819 695 describes a process for the modification of the rac/meso ratio of a rac/meso
15 mixture of a stereorigid bridged metallocene compounds by subjecting the mixture to a selective decomposition in the presence of compounds having either acidic hydrogen atoms or reactive halogen atoms, such as water, methanol, chlorotrimethylsilane. With this process, one isomeric form is decomposed with a consequently lowering of the overall yield of the process.

WO 00/017213 describes an isomerization process in which the meso form or a mixture
20 of racemic and meso form of a bridged metallocene compound is contacted with a Group 1 and/or 2 metal halide isomerization catalyst in a liquid medium. This process has the drawback that the elimination of the metal halide from the reaction mixture could be complicated.

Organometallics 1998, 17, 1946-4958 describes a series of reactions in which rac-dimethylsilyl(1,3-diisopropylcyclopentadienyl)scandium allyl is isomerized to a rac/meso
25 mixtures by using different isomerization catalysts. Among all (n-C₇H₁₅)₄NCl and (n-C₇H₁₅)₄NBr are used. This isomerization reaction is obviously not useful for an industrial process which target is to obtain the rac isomer. Moreover, on page 4953 of this document it is stated that the isomerization is discouraged for metallocenes of group 4, thus creating a prejudice in using this kind of reaction with metallocene compounds in which the central metal belongs to
30 group 4 of the periodic table of the elements.

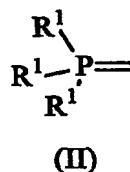
Thus it is desirable to find an alternative isomerization process that allows isomerizing the meso or meso-like form of a bridged metallocene compounds in the rac or rac-like form in an easy way.

- 5 An object of the present invention is an isomerization process comprising the step of contacting a slurry or a solution comprising the meso or meso-like form of one or more bridged metallocene compounds of group 4 of the Periodic Table of the Elements having C₂ or C₂-like symmetry with an isomerization catalyst of formula (I)



wherein:

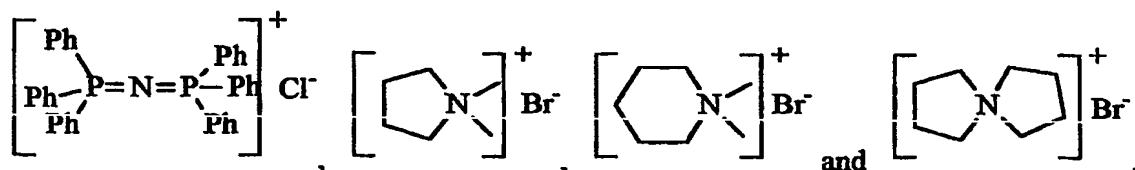
- 10 W is a nitrogen or a phosphorus atom; preferably W is nitrogen;
R, equal to or different from each other, are C₁-C₄₀ hydrocarbon radicals optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; two R can also join to form a saturated or unsaturated C₅-C₆ membered cycle containing the atom W to form for example a pyrrolyl, a pirrolydiny or a pyperidiny radical or two R can also join to
15 form a radical of formula (II)



- wherein R¹, equal to or different from each other, are C₁-C₂₀ hydrocarbon radicals optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R¹ are linear or branched, cyclic or acyclic, C₁-C₁₂-alkyl, C₂-C₁₂ alkenyl, C₂-C₁₂ alkynyl, C₆-C₁₂-aryl, C₇-C₁₂-alkylaryl or C₇-C₁₂-arylalkyl radicals; P is a phosphorous atom
20 bonded with a double bond to the atom W; preferably R are linear or branched, cyclic or acyclic, C₁-C₄₀-alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₆-C₄₀-aryl, C₇-C₄₀-alkylaryl or C₇-C₄₀-arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;
more preferably R is a C₁-C₄₀-alkyl, C₆-C₄₀-aryl or C₇-C₄₀-alkylaryl radical, such as n-butyl, n-
25 hexyl, phenyl and benzyl (Bz) radicals; and
X⁻ is an halide atom such as Cl⁻, Br⁻, I⁻, F⁻, preferably X⁻ is chloride (Cl⁻) or bromide (Br⁻).

Examples of compounds of formula (I) are (CH₃(CH₂)₃)₄NBr, (CH₃(CH₂)₅)₄NBr,

$(\text{CH}_3\text{CH}_2)_3(\text{C}_6\text{H}_5\text{CH}_2)\text{NBr}$, $(\text{CH}_3(\text{CH}_2)_3)_4\text{NCl}$, $(\text{CH}_3\text{CH}_2)_3(\text{C}_6\text{H}_5\text{CH}_2)\text{NCl}$, $(\text{CH}_3(\text{CH}_2)_3)_4\text{PBr}$,
 $(\text{CH}_3(\text{CH}_2)_5)_4\text{PBr}$, $(\text{CH}_3\text{CH}_2)_3(\text{C}_6\text{H}_5\text{CH}_2)\text{PBr}$, $(\text{CH}_3(\text{CH}_2)_3)_4\text{PCl}$, $(\text{CH}_3\text{CH}_2)_3(\text{C}_6\text{H}_5\text{CH}_2)\text{PCl}$,

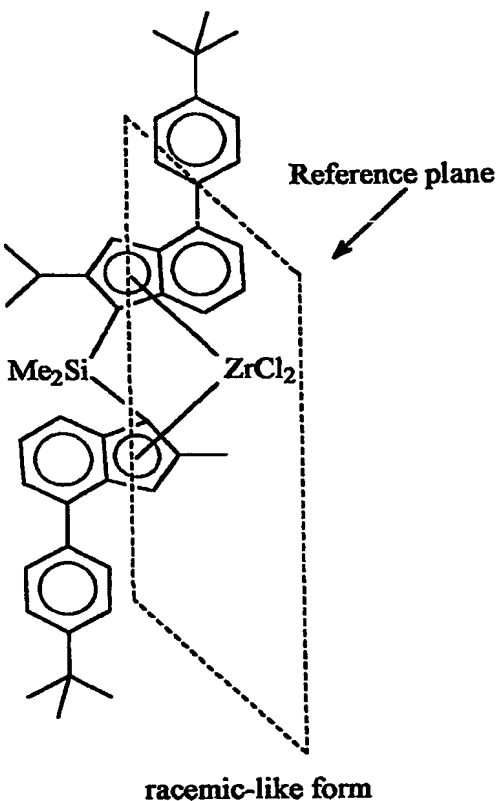


The bridged metallocene compounds of group 4 of the Periodic Table of the Elements having C_2 or C_2 -like symmetry have two bridged cyclopentadienyl moieties linked to the central metal atom through a π bond. The central metal atom is zirconium, titanium or hafnium, preferably zirconium.

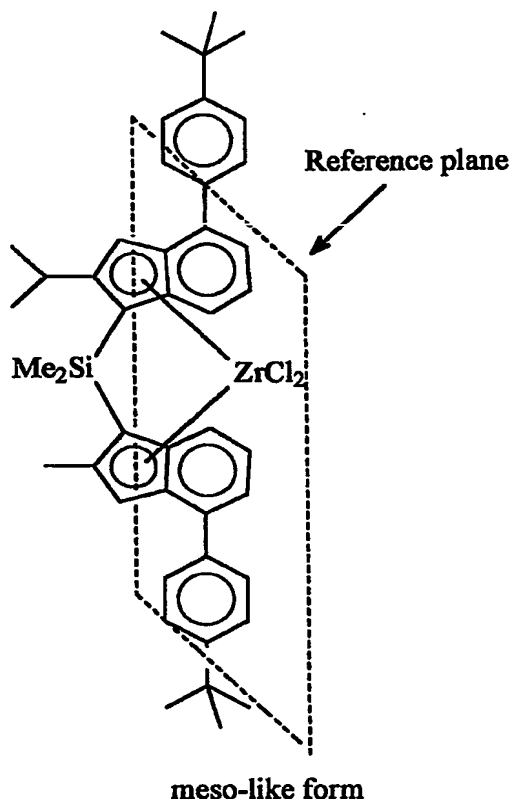
- 5 For the purpose of the present invention, the term " C_2 symmetry" means that in the metallocene compound two isomeric forms are possible, the racemic and the meso forms. These isomeric forms are well known in the art for example they are cited in *Chem. Rev.* 2000, 100, 1253-1345.

- 10 For the purpose of the present invention, the term " C_2 -like symmetry" means that in the metallocene compound two isomeric forms are possible, the racemic-like and the meso-like form.

- 15 "Racemic-like form" means that the bulkier substituents of the two cyclopentadienyl moieties on the metallocene compound are on the opposite sides with respect to the plane containing the zirconium and the centre of the cyclopentadienyl moieties as shown in the following compound.



- Conversely meso-like form means that the bulkier substituents of the two cyclopentadienyl moieties on the metallocene compound are on the same side with respect to the plane containing the zirconium and the centre of the cyclopentadienyl moieties as shown in the following compound.
- 5



With the process of the present invention the meso or meso-like form of one or more bridged metallocene compounds of group 4 of the Periodic Table of the Elements having C_2 or C_2 -like symmetry can be used alone or in a mixture comprising the racemic or racemic-like form.

5 According to a preferred embodiment, the process of the present invention is carried out in an aprotic solvent, either polar or apolar. Said aprotic solvent can be an aromatic or aliphatic hydrocarbon, optionally halogenated or optionally containing heteroatoms belonging to the group 16 of the periodic table, or an ether. Preferably it is selected from the group consisting of benzene, toluene, pentane, hexane, heptane, cyclohexane, dichloromethane, chlorobenzene, diethylether, 10 tetrahydrofuran, 1,2 dimethoxyethane N,N-dimethylformamide, dimethyl sulfoxide or mixtures thereof. Preferably the process of the present invention is carried out in the presence of one or more ethers such as tetrahydrofuran or 1,2 dimethoxyethane; more preferably the solvent contains at least 5% by volume of one or more ethers.

15 The process of the present invention can be carried out at a temperature ranging from 0°C to a temperature below the temperature of decomposition of the bridged metallocene compound in the selected solvent, usually up to 180°C . Preferably the process of the present invention is carried out

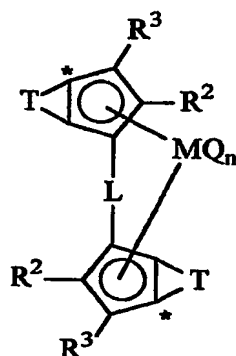
at a temperature ranging from 10°C to 150°C, more preferably from 30°C to 90°C, even more preferably from 40°C to 90°C.

The molar ratio between the isomerization catalyst and the metal of the bridged metallocene compound is preferably comprised between 0.01 to 300; more preferably the ratio is from 0.01 to 100, even more preferably from 0.1 to 10; particularly preferred ratio range is from 0.2 to 5.

With the process of the present invention it is possible to convert at least part of the meso or meso-like form to the racemic or racemic-like form of a bridged metallocene compound. This allows to improve the final yield in term of the racemic or racemic-like isomer of the whole process for synthesising the target metallocene compound. The removal of the isomerization catalyst and the final purification of the racemic or racemic like isomer can be carried out according to the procedure commonly used in the art.

The process of the present invention can be used as such or it can be part of a one-pot process for obtaining metallocene compounds starting from the ligands, such as the processes described in EP 03101268.5; WO 03/057705; WO 99/36427 and WO 02/083699.

Bridged metallocene compounds having C_2 symmetry or C_2 -like symmetry that can be used in the process of the present invention are preferably compounds of formula (III)



(III)

wherein:

M is a transition metal belonging to group 4, preferably M is zirconium, or hafnium;

the substituents Q, equal to or different from each other, are monoanionic sigma ligands selected from the group consisting of hydrogen, halogen, R^8 , OR^8 , $OCOR^8$, SR^8 , NR^8_2 and PR^8_2 , wherein R^8 is a linear or branched, cyclic or acyclic, C_1 - C_{20} -alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{20} -

aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radical optionally containing one or more Si or Ge atoms;

or two Q can optionally form a substituted or unsubstituted butadienyl radical or a OR'O group wherein R' is a divalent radical selected from C₁-C₂₀ alkylidene, C₆-C₄₀ arylidene, C₇-C₄₀

5 alkylarylidene and C₇-C₄₀ arylalkylidene radicals;

the substituents Q are preferably the same and are preferably halogen atoms, R⁸, OR⁸ and NR⁸₂; wherein R⁸ is preferably a C₁-C₁₀ alkyl, C₆-C₂₀ aryl or C₇-C₂₀ arylalkyl group, optionally containing one or more Si or Ge atoms; more preferably, the substituents Q are selected from the group consisting of -Cl, -Br, -Me, -Et, -n-Bu, -sec-Bu, -Ph, -Bz, -CH₂SiMe₃, -OEt, -OPr, -OBu, -OBz and
10 -NMe₂;

n is an integer equal to the oxidation state of the metal M minus 2;

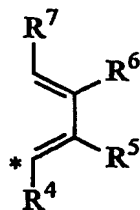
L is a divalent bridging group selected from C₁-C₂₀ alkylidene, C₃-C₂₀ cycloalkylidene, C₆-C₂₀ arylidene, C₇-C₂₀ alkylarylidene, or C₇-C₂₀ arylalkylidene radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, and silylidene radical
15 containing up to 5 silicon atoms such as SiMe₂, SiPh₂; preferably L is a divalent group (ZR⁹_m)_q; Z being C, Si, Ge, N or P, and the R⁹ groups, equal to or different from each other, being hydrogen or a linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radical or two R⁹ can form a aliphatic or aromatic C₄-C₇ ring; preferably R⁹ is a hydrogen atom or a methyl or phenyl radical; preferably Z is Si or C;

20 m is 1 or 2, and more specifically it is 1 when Z is N or P, and it is 2 when Z is C, Si or Ge; q is an integer ranging from 1 to 4; preferably q is 1 or 2;

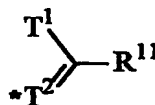
more preferably L is selected from Si(CH₃)₂, SiPh₂, SiPhMe, SiMe(SiMe₃), CH₂, (CH₂)₂, (CH₂)₃ or C(CH₃)₂;

R², R³, equal to or different from each other, are hydrogen atoms, halogen atoms or linear or
25 branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

T, equal to or different from each other, is a moiety of formula (IIIa) or (IIIb):



(IIIa)



(IIIb)

wherein:

the atom marked with the symbol * bonds the atom marked with the same symbol in the compound of formula (III);

T^1 is a sulphur atom, a oxygen atom or a CR^{10}_2 or a NR^{12} group, wherein R^{10} , equal to or different from each other, are hydrogen atoms, halogen atoms or linear or branched, cyclic or acyclic, C_1 - C_{20} -alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; and R^{12} is a or linear or branched, cyclic or acyclic, C_1 - C_{20} -alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably T^1 is sulphur.

T^2 is a CR^{10} group or a nitrogen atom; wherein R^{10} is a hydrogen atom, a halogen atom or linear or branched, cyclic or acyclic, C_1 - C_{20} -alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably T^2 is a CR^{10} group; with the proviso that if T^2 is a nitrogen atom T^1 is CR^{10}_2 ;

R^4 , R^5 , R^6 , R^7 , and R^{11} , equal to or different from each other, are hydrogen atoms, halogen atoms or linear or branched, cyclic or acyclic, C_1 - C_{20} -alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two adjacent R^4 , R^5 , R^6 , R^7 , R^{10} and R^{11} form one or more 3-7 membered ring optional containing heteroatoms belonging to groups 13-17 of the periodic table;

preferably R^2 and R^{11} , equal to or different from each other, are linear or branched C_1 - C_{20} -alkyl radicals, such as methyl, ethyl or isopropyl radicals;

preferably R^4 and R^{10} , equal to or different from each other, are hydrogen atoms or C_6 - C_{20} -aryl, or C_7 - C_{20} -arylalkyl radicals such as phenyl, 4-tert-butyl phenyl radicals.

Non limiting examples of compounds belonging to formula (I) are the following compounds;

- dimethylsilanediylbis(indenyl)zirconium dichloride,
- dimethylsilanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride,
- 5 dimethylsilanediylbis(4-naphthylindenyl)zirconium dichloride,
- dimethylsilanediylbis(2-methylindenyl)zirconium dichloride,
- dimethylsilanediylbis(2-methyl-4-t-butylindenyl)zirconium dichloride,
- dimethylsilanediylbis(2-methyl-4-isopropylindenyl)zirconium dichloride,
- dimethylsilanediylbis(2,4-dimethylindenyl)zirconium dichloride,
- 10 dimethylsilanediylbis(2-methyl-4,5-benzoidindenyl)zirconium dichloride,
- dimethylsilanediylbis(2,4,7-trimethylindenyl)zirconium dichloride,
- dimethylsilanediylbis(2,4,6-trimethylindenyl)zirconium dichloride,
- dimethylsilanediylbis(2,5,6-trimethylindenyl)zirconium dichloride,
- methyl(phenyl)silanediylbis(2-methyl-4,6-diisopropylindenyl)-zirconium dichloride,
- 15 methyl(phenyl)silanediylbis(2-methyl-4-isopropylindenyl)-zirconium dichloride,
- 1,2-ethylenebis(indenyl)zirconium dichloride,
- 1,2-ethylenebis(4,7-dimethylindenyl)zirconium dichloride,
- 1,2-ethylenebis(2-methyl-4-phenylindenyl)zirconium dichloride,
- 1,4-butanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride,
- 20 1,2-ethylenebis(2-methyl-4,6-diisopropylindenyl)zirconium dichloride,
- 1,4-butanediylbis(2-methyl-4-isopropylindenyl)zirconium dichloride,
- 1,4-butanediylbis(2-methyl-4,5-benzoidindenyl)zirconium dichloride,
- 1,2-ethylenebis(2-methyl-4,5-benzoidindenyl)zirconium dichloride,
- dimethylsilanediylbis-6-(3-methylcyclopentadienyl-[1,2-b]-thiophene) dichloride;
- 25 dimethylsilanediylbis-6-(4-methylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
- dimethylsilanediylbis-6-(4-isopropylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
- dimethylsilanediylbis-6-(4-tert-butylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
- dimethylsilanediylbis-6-(3-isopropylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
- dimethylsilanediylbis-6-(3-phenylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;

- dimethylsilanediylbis-6-(2,5-dichloride-3-phenylcyclopentadienyl-[1,2-b]-thiophene)zirconium dimethyl;
- dimethylsilanediylbis-6-[2,5-dichloride-3-(2-methylphenyl)cyclopentadienyl-[1,2-b]-thiophene]zirconium dichloride;
- 5 dimethylsilanediylbis-6-[2,5-dichloride-3-(2,4,6-trimethylphenyl)cyclopentadienyl-[1,2-b]-thiophene]zirconium dichloride;
- dimethylsilanediylbis-6-[2,5-dichloride-3-mesitylenecyclopentadienyl-[1,2-b]-thiophene]zirconium dichloride;
- dimethylsilanediylbis-6-(2,4,5-trimethyl-3-phenylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
- 10 dimethylsilanediylbis-6-(2,5-diethyl-3-phenylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
- dimethylsilanediylbis-6-(2,5-diisopropyl-3-phenylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
- 15 dimethylsilanediylbis-6-(2,5-diter-butyl-3-phenylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
- dimethylsilanediylbis-6-(2,5-ditrimethylsilyl-3-phenylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
- dimethylsilanediylbis-6-(3-methylcyclopentadienyl-[1,2-b]-silole)zirconium dichloride;
- 20 dimethylsilanediylbis-6-(3-isopropylcyclopentadienyl-[1,2-b]-silole)zirconium dichloride;
- dimethylsilanediylbis-6-(3-phenylcyclopentadienyl-[1,2-b]-silole)zirconium dichloride;
- dimethylsilanediylbis-6-(2,5-dichloride-3-phenylcyclopentadienyl-[1,2-b]-silole)zirconium dichloride;
- dimethylsilanediylbis-6-[2,5-dichloride-3-(2-methylphenyl)cyclopentadienyl-[1,2-b]-silole]zirconium dichloride;
- 25 dimethylsilanediylbis-6-[2,5-dichloride-3-(2,4,6-trimethylphenyl)cyclopentadienyl-[1,2-b]-silole]zirconium dichloride;
- dimethylsilanediylbis-6-[2,5-dichloride-3-mesitylenecyclopentadienyl-[1,2-b]-silole]zirconium dichloride;
- 30 dimethylsilanediylbis-6-(2,4,5-trimethyl-3-phenylcyclopentadienyl-[1,2-b]-silole)zirconium dichloride;

Dimethylsilanediylbis(2-methyl-4-*p*-tert-butylphenylindenyl)zirconium dichloride;

Dimethylsilanediyl(2-isopropyl-4-*p*-tert-butylphenylindenyl)(2-methyl-4-*p*-tert-butylphenylindenyl)zirconium dichloride;

5 Dimethylsilanediyl(2-isopropyl-4-*p*-tert-butylphenylindenyl)(2-methyl-4-*p*-tert-butyl-7-methylphenylindenyl)zirconium dichloride;

as well as the corresponding zirconium dimethyl, hydrochloro dihydro and η^4 butadiene compounds.

The following examples are given to illustrate and not to limit the invention.

Examples

10 Dimethylsilanediyl [2-methyl-4-(4'-*tert*-butylphenyl)indenyl] [2-isopropyl-4-(4'-*tert*-butylphenyl)indenyl] dimethyl zirconium (A) is prepared following the same procedure described in example 5 of PCT/EP02/14899 by using [2-methyl-4-(4'-*tert*-butylphenyl)indenyl] [2-isopropyl-4-(4'-*tert*-butylphenyl)indenyl]dimethylsilane instead of bis(2-methylindenyl)dimethylsilane.

15 Dimethylsilanediylbis[2-methyl-4,5-benzo-1-indenyl] dimethyl zirconium (B) was prepared according to US 6,177,376.

Dimethylsilanediylbis[2-methyl-4,5-benzo-1-indenyl] zirconium dichloride (C) was prepared according to US 5,830,821.

Examples 1-7 General procedure.

20 A purified *meso* enriched metallocene was dissolved (or slurried) at room temperature in the solvent indicated in table 1. The isomerization catalyst specified in table 1 was added and then the mixture was heated for few hours. NMR analysis of a sample of the resulting solution (or slurry) showed that the *rac/meso* ratio of the metallocene was substantially improved in favour of the *rac* isomer. The latter was also isolated in higher yields compared with the yields
25 achieved by using standard procedures.

The *rac/meso* ratios were determined by NMR analysis. The proton spectra of metallocenes were obtained on a Bruker DPX 200 spectrometer operating in the Fourier transform mode at room temperature at 200.13 MHz. The samples were dissolved in CD₂Cl₂ (Aldrich, 99.8 atom % D); preparation of the samples was carried out under nitrogen using
30 standard inert atmosphere techniques. The residual peak of CHDCl₂ in the ¹H spectra (5.35

ppm) was used as a reference. Proton spectra were acquired with a 15° pulse and 2 seconds of delay between pulses; 32 transients were stored for each spectrum.

Table 1							
Ex.	Met.	starting <i>rac/meso</i> ratio	Isomerization catalyst (n° eq./Zr)	Solvent	T (°C)	t (h)	final <i>rac/meso</i> ratio
1	A	2.4/97.6	<i>n</i> -Bu ₄ NBr (0.22/1)	THF	65	5	94.0/6.0
2	A	31.7/68.3	<i>n</i> -Bu ₄ NBr (0.21/1)	toluene, T HF 1/1.7 v/v	80	4	78.9/21.1
3	A	31.7/68.3	[CH ₃ (CH ₂) ₅] ₄ NBr (0.23/1)	toluene, T HF 1/1.7 v/v	80	10	76.5/23.5
4	A	31.7/68.3	(CH ₃ CH ₂) ₃ BzNCl (0.23/1)	toluene, T HF 1/1.7 v/v	80	4	75.2/24.8
5	B	26.8/73.2	<i>n</i> -Bu ₄ NBr (0.22/1)	THF	65	2	71.9/28.1
6	C	17.7/82.3	<i>n</i> -Bu ₄ NBr (0.23/1)	THF	65	2.5	94.4/5.6
7	A	33.3/66.7	<i>n</i> -Bu ₄ NBr (0.21/1)	chloroben zene	80	7.5	70.4/29.6
8	A	33.3/66.7	Et ₃ BzNCl (0.21/1)	toluene	80	3	61.5/38.5

note:

no remarkable amount of decomposition was observed.

5

Et = ethyl radical *n*-Bu = normal butyl radical; Bz = benzil radical

Comparative example 1.

A sample of ammonium chloride (Aldrich, MW 53.49) was dried at 125°C for 8 h under vacuum. An aliquot of this sample (Aldrich, 17.0 mg, 0.32 mmol, $\text{NH}_4\text{Cl}/\text{dimethyl complex} = 0.20/1$) was added at room temperature under nitrogen atmosphere to a solution of 1.16 g of dimethylsilanediyl[2-methyl-4-(4'-*tert*-butylphenyl)indenyl][2-isopropyl-4-(4'-*tert*-butylphenyl)indenyl] dimethyl zirconium (*rac/meso* 31.7/68.3, MW = 728.26, 1.59 mmol) in 25 mL of THF and 15 mL of toluene in a 50 mL Schlenk flask. At the end of the addition, the reaction mixture was heated at 80°C for 2.5 h and followed by NMR analysis: the *rac/meso* ratio resulted to be 34/66 and a small amount of decomposition to the ligand was also observed.

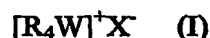
Additional ammonium chloride (100.0 mg, 1.87 mmol, total $\text{NH}_4\text{Cl}/\text{dimethyl complex} = 1.38/1$) was added at room temperature and then the resulting mixture was heated at 80°C for 3.5 h. Different aliquots of the mixture were taken, dried and analysed by ^1H NMR in CD_2Cl_2 . The final *rac/meso* ratio resulted to be 45/55 and a remarkable amount of decomposition to the ligand (ca. 20% mol. calculated by NMR) was also observed.

Comparative example 2.

A sample of triethylamine hydrochloride (Aldrich, 98%, MW 137.65, 25.7 mg, 0.18 mmol, $\text{NHEt}_3\text{Cl}/\text{dimethyl complex} = 0.22/1$) was suspended at room temperature into 5 mL of THF and added under nitrogen atmosphere to a suspension of 0.58 g of dimethylsilanediyl[2-methyl-4-(4'-*tert*-butylphenyl)indenyl][2-isopropyl-4-(4'-*tert*-butylphenyl)indenyl] dimethyl zirconium (*rac/meso* 30/70, MW = 728.26, 0.80 mmol) in 15 mL of THF in a 50 mL Schlenk flask. At the end of the addition, the reaction mixture was heated at reflux for 2 h and followed by NMR analysis: the *rac/meso* ratio resulted to be 45/55, but a remarkable amount of decomposition was also observed. The heating was then continued for additional 2 h, but no change in the *rac/meso* ratio was observed by NMR analysis.

CLAIMS

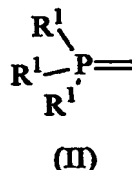
1. An isomerization process comprising the step of contacting a slurry or a solution comprising the meso or meso-like form of one or more bridged metallocene compounds of group 4 of the Periodic Table of the Elements having C_2 or C_2 -like symmetry with an isomerization catalyst of formula (I)



wherein:

W is a nitrogen or a phosphorus atom;

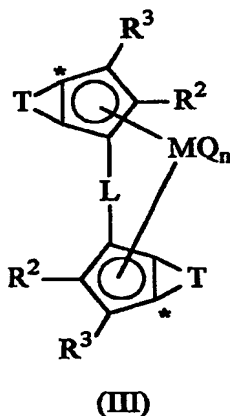
- 10 R, equal to or different from each other, are C_1 - C_{40} hydrocarbon radicals optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; two R can also join to form a saturated or unsaturated C_5 - C_6 membered cycle containing the atom W or two R can also join to form a radical of formula (II)



- 15 wherein R^1 , equal to or different from each other, are C_1 - C_{20} hydrocarbon radicals optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; P is a phosphorous atom bonded with a double bond to the atom W; and X is an halide atom.

- 20 2. The isomerization process according to claim 1 wherein a mixture comprising the meso or meso-like form and the racemic or racemic-like form of one or more bridged metallocene compounds of group 4 of the Periodic Table of the Elements having C_2 or C_2 -like symmetry is used.
- 25 3. The isomerization process according to claims 1-2 wherein R are linear or branched, cyclic or acyclic, C_1 - C_{40} -alkyl, C_2 - C_{40} alkenyl, C_2 - C_{40} alkynyl, C_6 - C_{40} -aryl, C_7 - C_{40} -alkylaryl or C_7 - C_{40} -arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; two R can also join to form a saturated or unsaturated C_5 - C_6 membered cycle containing the atom W; and X is chloride (Cl⁻) or bromide (Br⁻).

4. The isomerization process according to anyone of claims 1-3 wherein W is a nitrogen atom.
5. The isomerization process according to anyone of claims 1-4 wherein the process is carried out in an aprotic solvent, either polar or apolar.
- 5 6. The isomerization process according to claim 5 wherein the aprotic solvent is an aromatic or aliphatic hydrocarbon, optionally halogenated or optionally containing heteroatoms belonging to the group 16 of the periodic table, or an ether.
7. The isomerization process according to claim 6 wherein the process is carried out in the presence of one or more ethers.
- 10 8. The isomerization process according to anyone of claims 1-7 wherein the process is carried out at a temperature ranging from 0 to a temperature below the temperature of decomposition of the bridged metallocene compound in the selected solvent.
9. The isomerization process according to anyone of claims 1-8 wherein the bridged metallocene compounds having C_2 symmetry or C_2 -like symmetry has formula (III)



15 wherein:

M is a transition metal belonging to group 4,

the substituents Q, equal to or different from each other, are monoanionic sigma ligands selected from the group consisting of hydrogen, halogen, R^8 , OR^8 , $OCOR^8$, SR^8 , NR^8_2 and PR^8_2 , wherein R^8 is a linear or branched, cyclic or acyclic, C_1 - C_{20} -alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radical optionally containing one or more Si or Ge atoms;

20

or two Q can optionally form a substituted or unsubstituted butadienyl radical or a $OR'O$ group wherein R' is a divalent radical selected from C_1 - C_{20} alkylidene, C_6 - C_{40} arylidene, C_7 -

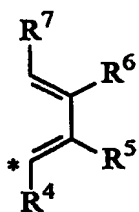
C₄₀ alkylarylidene and C₇-C₄₀ arylalkylidene radicals;

n is an integer equal to the oxidation state of the metal M minus 2;

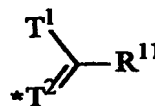
L is a divalent bridging group selected from C₁-C₂₀ alkylidene, C₃-C₂₀ cycloalkylidene, C₆-C₂₀ arylidene, C₇-C₂₀ alkylarylidene, or C₇-C₂₀ arylalkylidene radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, and silylidene radical containing up to 5 silicon atoms;

R², R³, equal to or different from each other, are hydrogen atoms, halogen atoms or linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

T, equal to or different from each other, is a moiety of formula (IIIa) or (IIIb):



(IIIa)



(IIIb)

wherein:

the atom marked with the symbol * bonds the atom marked with the same symbol in the compound of formula (III);

T¹ is a sulphur atom, a oxygen atom or a CR¹⁰₂ or a NR¹² group, wherein R¹⁰, equal to or different from each other, are hydrogen atoms, halogen atoms or linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; and R¹² is a or linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

T² is a CR¹⁰ group or a nitrogen atom; wherein R¹⁰ is a hydrogen atom, a halogen atom or linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-

aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

with the proviso that if T² is a nitrogen atom T¹ is CR¹⁰₂;

R⁴, R⁵, R⁶, R⁷, and R¹¹, equal to or different from each other, are hydrogen atoms, halogen

- 5 atoms or linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two adjacent R⁴, R⁵, R⁶, R⁷, R¹⁰ and R¹¹ form one or more 3-7 membered ring optional containing heteroatoms belonging to groups 13-17 of the periodic table.

- 10 10. The isomerization process according to claim 9 wherein in the compound of formula (III) M is zirconium, or hafnium; the substituents Q are the same and are halogen atoms, R⁸, OR⁸ and NR⁸₂; wherein R⁸ is preferably a C₁-C₁₀ alkyl, C₆-C₂₀ aryl or C₇-C₂₀ arylalkyl group, optionally containing one or more Si or Ge atoms; L is a divalent group (ZR⁹_m)_q; Z being C, Si, Ge, N or P, and the R⁹ groups, equal to or different from each other, being hydrogen or a
- 15 linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radicals or two R⁹ can form a aliphatic or aromatic C₄-C₇ ring.
11. The isomerization process according to claims 9-10 wherein in the compound of formula (II) R² and R¹¹, equal to or different from each other are linear or branched C₁-C₂₀-alkyl
- 20 radicals; R⁴ and R¹⁰, equal to or different from each other, are hydrogen atoms or C₆-C₂₀-aryl, or C₇-C₂₀-arylalkyl radicals; T¹ is sulphur and T² is a CR¹⁰ group.

Abstract

An isomerization process comprising the step of contacting a slurry or a solution comprising the meso or meso-like form of one or more bridged metallocene compounds of group 4 of the Periodic Table of the Elements having C₂ or C₂-like symmetry with an isomerization catalyst of formula (I)



wherein:

W is a nitrogen or a phosphorus atom; R, equal to or different from each other, are C₁-C₄₀ hydrocarbon radicals and X⁻ is an halide atom.

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